

Effect of Calcination Temperatures on Microstructure and Phase Formation of $\text{Ba}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3$

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ABSTRACT

In this work, the effect of calcination temperatures on microstructure and phase formation of $\text{Ba}(\text{Zr}_{0.3}\text{Ti}_{0.7})\text{O}_3$ (BZT) powders was investigated. The BZT powders were prepared via the solid state reaction method under various calcination temperatures. The thermal gravimetric (TG) differential thermal analysis (DTA) and X-ray diffraction (XRD) were evaluated the optimum condition for calcinations. The microstructure was studied by using scanning electron microscopy (SEM). It has been found that the second phases such as BaCO_3 , ZrO_2 , BaZrO_3 and Ba_2ZrO_4 were existed with calcination temperature below 1200 °C. The pure perovskite phase of the BZT powders was obtained with calcination condition at 1300 °C for 4 h. Lattice parameter (a) tended to increased with increasing calcinations temperatures. The percentage of cubic perovskite phase was discussed. The TG-DTA results were corresponding to XRD investigation. The microstructures of the powders exhibited an almost-spherical morphology and have a porous agglomerated form. The average particle sizes were increased from 0.23 to 1.13 μm with increasing of calcinations temperatures from 800 to 1350 °C, respectively.

Keywords: barium zirconate titanate, microstructure, phase formation, solid state reaction

INTRODUCTION

Barium titanate (BaTiO_3 , BT) is well known as a fundamental ferroelectric perovskite oxide (Clabaugh *et al.*, 1956) and is often used in multilayer ceramic capacitors (MLCs) due to a high dielectric constant (Sakabe *et al.*, 1981). BaTiO_3 displays dielectric anomalies at 130, 0, and -90 °C with respective transformations in symmetry from cubic to tetragonal, from tetragonal to orthorhombic, and from orthorhombic to rhombohedral, respectively. Those anomalies accompany a high dielectric constant near the phase transition (Jaffe *et al.*, 1997). The nature and phase transition temperature of BT can be modified via partial substitution of either Ba ions (A-site doping) or Ti ions (B-site doping). A-site doping with cations of the same valence as Ba cause the Curie temperature (T_c) (~ 130 °C) to either decrease (Sr substitution) or increase (Pb substitution) without any significant broadening of the transition (Nemoto *et al.*, 1980). With B-site doping, the ferroelectric domains, which are associated with a cooperative off-center displacement of Ti^{4+} ions in their

TiO₆ octahedra, are disrupted, which often leads to broadening of the transition at T_c. Partial replacement of titanium by tin, or hafnium generally leads to a reduction in T_c and an increase in the permittivity maximum with dopant content (Kuwabara *et al.*, 1996).

Barium zirconate titanate (Ba(Ti_{1-x}Zr_x)O₃, BZT) is obtained by substituting ions at B site of BaTiO₃ with Zr ions. This substitution results in a decrease of the temperature of permittivity maximum and a broadening of the maximum (Ulrich *et al.*, 2001). Brajer and Kulscar showed that, as the zirconium content increases, the orthorhombic-tetragonal phase transition temperature increase and the tetragonal-cubic phase transition temperature decreases (Brajer *et al.*, 1955; Kulscar *et al.*, 1956). At a Zr/Ti ratio greater than 0.10, the three dielectric constant peaks coalesce into a single broad maximum (Hennings *et al.*, 1982). Moreover, the transition temperature of BZT shifting to a lower temperature region with increasing Zr content. The dielectric study of the Ba(Ti_{1-x}Zr_x)O₃ ceramics with 0.20 ≤ x ≤ 0.35 showed a normal ferroelectric with a weak diffuse phase transition behaviors for the ceramics with x=0.20 and 0.25 (Tang *et al.*, 2004). The diffuse phase transition and a relaxor-like behavior were found at high Zr contents (x=0.30 and 0.35). The tunability and the dielectric loss of the Ba(Ti_(1-x)Zr_x)O₃ with x=0.3 ceramic measured at room temperature under the biasing field 40 kV/cm are 45% and 0.002, respectively (Tang *et al.*, 2004; Yu *et al.*, 2002). This make the Ba(Ti_{0.7}Zr_{0.3})O₃ ceramic promising material for tunable materials applications. However, to the author's best knowledge no prepared powder studies by solid state reaction method have reported yet. Therefore, in the present work, the effect of calcinations temperature on prepared via solid state reaction method was studied.

EXPERIMENTAL PROCEDURE

The starting materials were commercially available barium carbonate, BaCO₃ (99%) titanium (IV) oxide, TiO₂ (99%) and zirconium (IV) oxide, ZrO₂ (99%). Barium zirconate titanate (Ba(Zr_{0.25}Ti_{0.75})O₃, BZT) powder was synthesized by the solid state reaction of thoroughly ground mixtures of BaCO₃, TiO₂ and ZrO₂ powder that were milled in the required stoichiometric ratio. Instead of employing a ball milling procedure (zirconia milling media under ethanol for 24 h) drying was carried out at 120 °C for 4 h, prior to sieving. After sieving, various calcination temperatures ranging from 800 to 1350 °C, dwell time 4 h and heating/cooling rate 5 °C/min. The reaction of the uncalcined BZT powder taking place during heat treatment were investigated by thermogravimetric and differential thermal analysis (TG-DTA; PerkinElmer 7 series thermal analysis) using a heating rate of 10 °C/min in air from room temperature up to 1,350 °C. Calcined powders were subsequently examined by room temperature X-ray diffraction (XRD; Philip PW3040/60 X' Pert Pro) to identify the phase formed and optimum calcination temperature of BZT powders. Powder morphologies and particle sizes were directly image, using scanning electron microscopy (SEM; LEO 1455 VP).

RESULTS AND DISCUSSION

The TG-DTA curves recorded at a heating rate of 10 °C/min in air for an equimolar mixture in the stoichiometric proportion of BZT is displayed in figure 1. The TG curve shows two distinct weight losses. The first weight loss occurs around 780 °C and the second one above 1180 °C. The sample shows a small exothermic peak in the DTA curve ~108 °C. This DTA peak can be attributed to the vaporization of water. No anomaly was observed from the TG pattern at this temperature. This may indicate that the small amount of vaporization of water could not be detected by the TG measurement. The first weight loss is attributed to the transition from witherite orthorhombic BaCO₃ to the rhombohedral phase (Simon *et al.*, 2006). In the second fall in specimen weight, the solid state reaction between BaCO₃, TiO₂ and ZrO₂ was observed. The broad endothermic characteristic in the DTA curve represents that reaction which has a minimum at 908 °C. Moreover, another endothermic peak with a minimum at 1278 °C was also observed in this profile. These data were used to define the range of calcination temperatures from 800 to 1350 °C for XRD investigation.

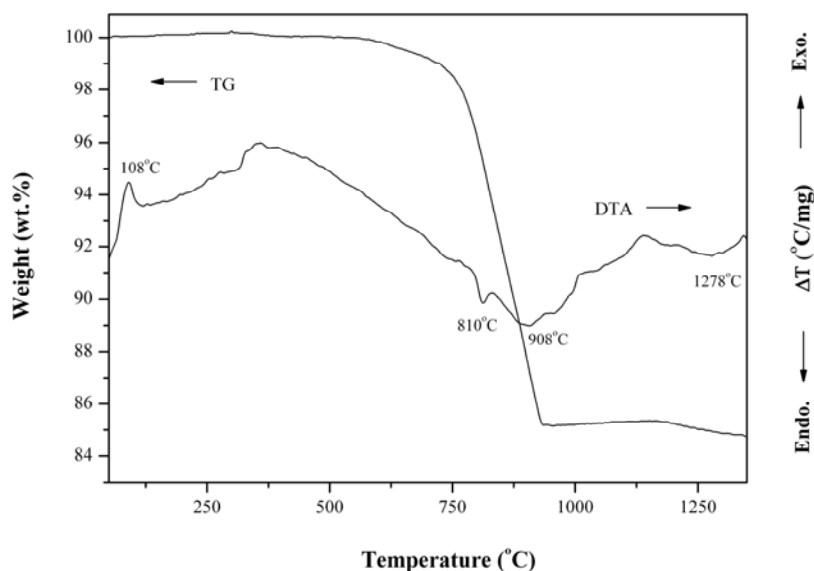


Figure 1 TG and DTA curves for the mixture of BaCO₃-TiO₂-ZrO₂ powder.

To further study the phase development with increasing calcination temperatures in the powder, they were calcined for 4 h in air at various temperatures up to 1350 °C, followed by phase analysis using XRD. The XRD patterns of the BZT powders formed at various calcination are given in figure 2. After calcination at 800 °C, crystalline phase of BZT was accompanied with BaCO₃ and ZrO₂ as separate phases, which X-ray peak of the residue materials could be matched with JCPDS file number 41-0373 and 24-1165 respectively. As the temperature increased

to 1000 °C, the peaks corresponding to raw materials disappeared, while the intensity of BaZrO₃ and Ba₂ZrO₄ peaks become the minor phase, which can be correlated with JCPDS file number 06-0399 and 24-0130 respectively. Furthermore, the XRD pattern of 1000 °C calcination sample also presented a small peak of unknown phase. After calcination at 1250 °C, the peak corresponding to BaZrO₃ and Ba₂ZrO₄ was not detectable, whereas the unknown phase could not be eliminated. However, a single phase of BZT is already formed was calcined at 1300 °C. This observation agrees well with those derived from the TG-DTA results.

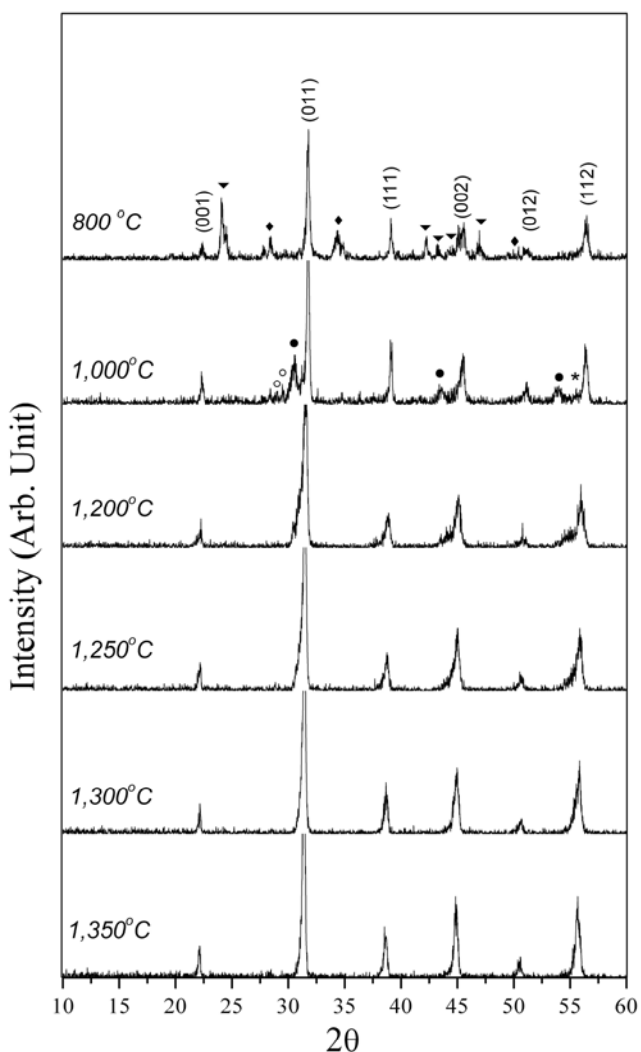


Figure 2 XRD patterns of Ba(Zr_{0.25}Ti_{0.75})O₃ powder were prepared by solid state reaction: (▼) BaCO₃; (◆) ZrO₂; (●) BaZrO₃; (○) Ba₂ZrO₄; (*) unknown.

The strongest reflections in the majority of the XRD patterns indicate formation of the perovskite phase of BZT, which could be matched with JCPDS file number 36-0019. To a first approximation, this phase has a cubic perovskite type structure in space group Pm-3m (no.221) with cell parameter $a = 4.0520 \text{ \AA}$. The lattice parameter as a function of calcination temperatures of this study shows in figure 3. The lattice parameter was increased with increasing of calcinations temperatures. This indicated that the calcination temperatures have direct significance to lattice parameter and unit cell volume.

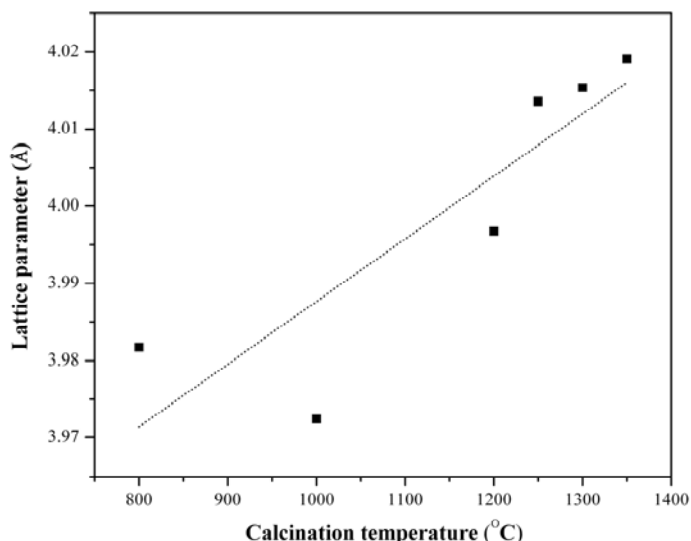


Figure 3 Lattice parameter of BZT powders calcined at different temperatures.

The relative amount of perovskite and impurity phases were determined by measuring the major XRD peak intensities of the perovskite and impurity phases. The percentage of perovskite phase was estimated by the following equation

$$\% \text{perovskite phase} = \left(\frac{I_{\text{perov}}}{I_{\text{perov}} + I_{\text{BaZrO}_3} + I_{\text{Ba}_2\text{ZrO}_4} + I_{\text{unknown}}} \right) \times 100$$

This equation is well-known equation widely employed in connection with the preparation of complex perovskite structure materials (Vittayakorn *et al.*, 2003, Vittayakorn *et al.*, 2004). Here I_{perov} , I_{BaZrO_3} , $I_{\text{Ba}_2\text{ZrO}_4}$ and I_{unknown} refer to the intensity of the (011) perovskite peak, intensities of the highest BaZrO_3 , Ba_2ZrO_4 and unknown respectively.

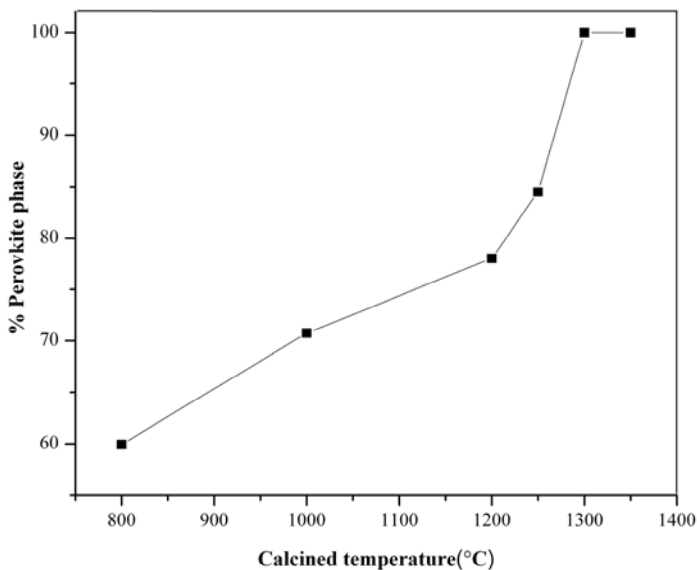


Figure 4 Perovskite phase content in BZT powders calcined at different temperatures.

Figure 4 shows the percent perovskite phase of BZT as a function of calcinations temperature. The perovskite phase of 800 to 1250 °C calcined samples is not reached hundred percent. Whilst, the single phase of perovskite of the higher 1300 °C calcined samples is formed. The percentage of BZT perovskite phase was increased with increasing of calcination temperatures.

SEM photomicrograph of BZT powder calcined between 800 and 1350 °C showed in figure 5. These powders exhibit an almost spherical morphology and have a porous agglomerated form. As the temperature increased, more agglomerate particles could be observed. The average particle sizes tend to increase with calcination temperatures as shown in figure 6. The average particle sizes were 0.23, 0.31, 0.62, 0.76, 0.89 and 1.13 μm with the calcination temperatures 800, 1000, 1200, 1250, 1300, 1350 °C, respectively.

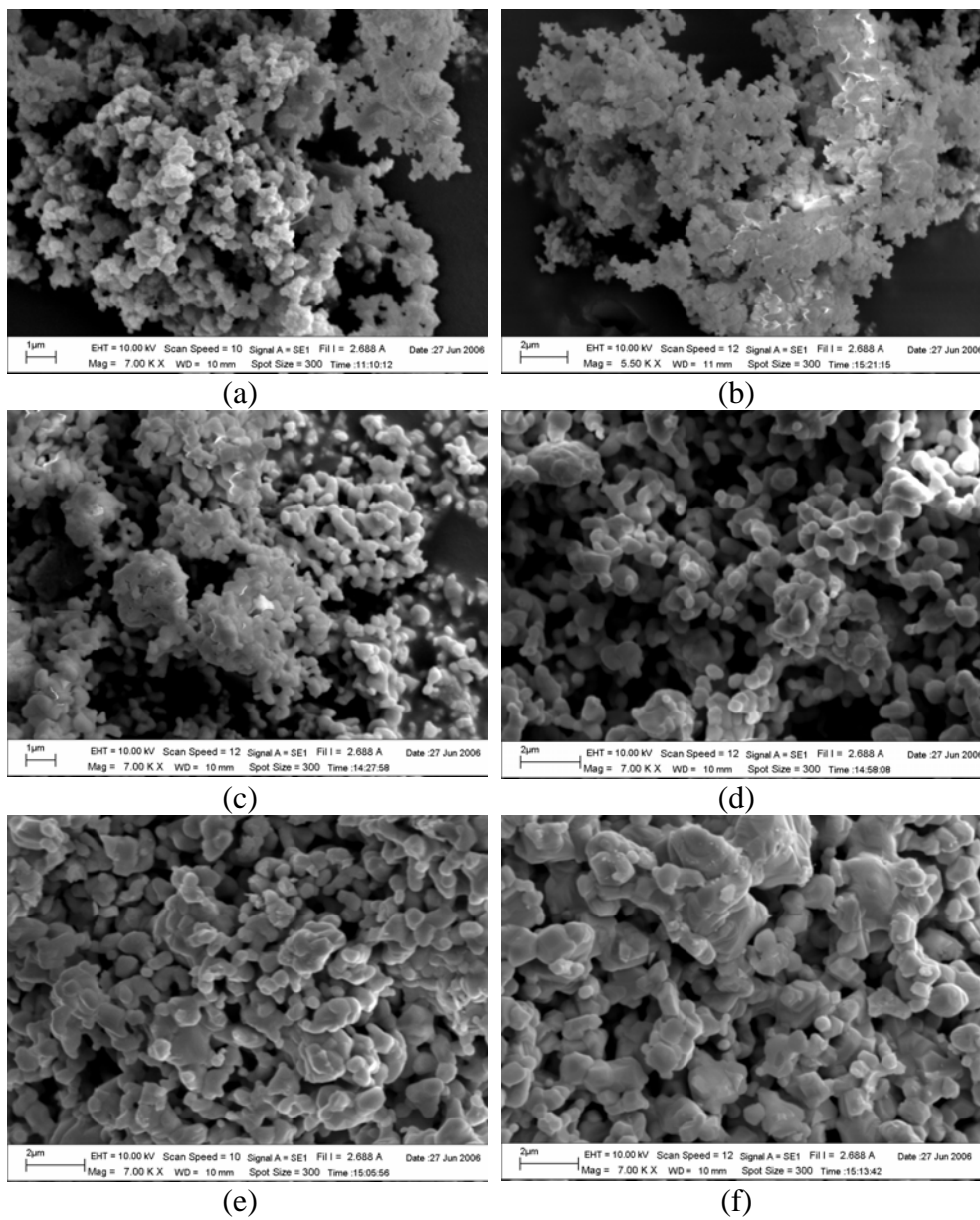


Figure 5 SEM photomicrograph of BZT powders calcined at (a) 800 °C, (b) 1000 °C, (c) 1200 °C, (d) 1250 °C, (e) 1300 °C and (f) 1350 °C.

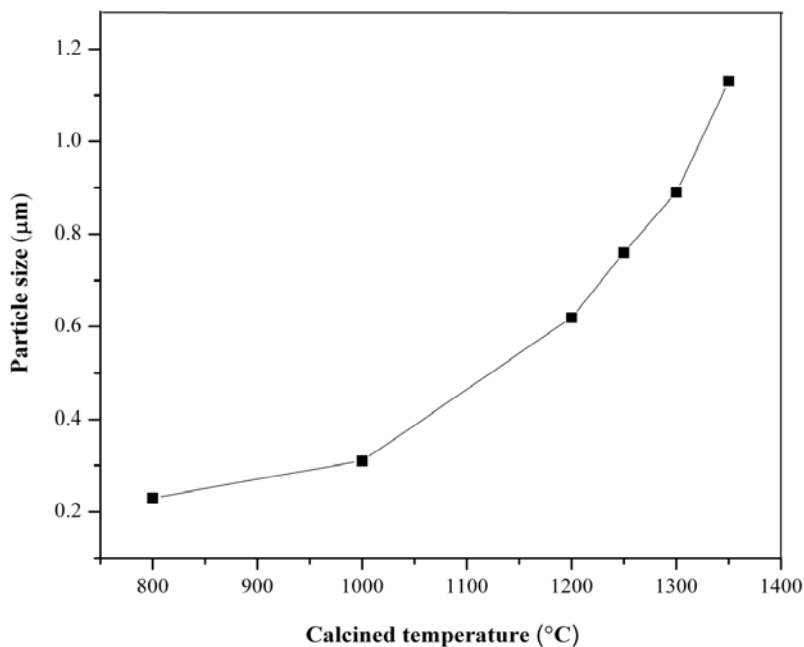


Figure 6 Average particle size of BZT powders calcined at different temperatures.

CONCLUSION

It has been shown that pure $\text{Ba}(\text{Ti}_{0.7}\text{Zr}_{0.3})\text{O}_3$ powders can be formed by the reaction of barium carbonate, titanium (IV) oxide and zirconium (IV) oxide via calcined temperature at 1300 °C. Evidence for the formation of BaZrO_3 , Ba_2ZrO_4 minor phase and unknown phase, which coexists with the perovskite phase, is found at calcinations temperatures ranging from 1000-1250 °C. The calcination temperature has a strong influence on the crystal structure, homogeneity and the unit cell volume of the calcined powders. The resulting BZT powders presented more agglomerated as the calcination temperature increased.

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REFERENCES

- Brajer, E. J. (1955). *Polycrystalline Ceramic materials*, U.S. Pat, No. 2 708 243.
- Clabaugh, W.S., Swiggard, R. and Gilchrist, R. (1956). Preparation of barium titanyl oxalate tetrahydrate for conversion to barium titanate of high purity. *J. Res. Nat. Bur. Stds.*, 56, 289.
- Hennings, D., Schnell, A. and Simon, G. (1982). Diffuse ferroelectric phase transitions in $Ba(Ti_{1-y}Zr_y)O_3$ ceramics. *J. Am. Ceram. Soc.*, 65(11), 539.
- Jaffe, B., Cook Jr., W. R. and Jaffe, H. (1997). *Piezoelectric ceramics, in nonmetallic solid: series of monographs No.3*. Academic Press, London, U.K., 53.
- Kulscar, F. (1956). *Fired ceramic barium titanate body*, U.S. Pat, No. 2 735 024.
- Kuwabara, M., Morimo, K. and Matsunaga, T. (1996). Singer-grain boundaries in PCT resistors. *J. Am. Ceram. Soc.*, 79(4), 997.
- Nemoto, H. and Oda, I. (1980). Direct examinations of PTC action of single grain boundaries in semiconducting $BaTiO_3$ ceramics. *J. Am. Ceram. Soc.*, 63(7-8), 398.
- Sakabe, Y., Minai, K. and Wakino, K. (1981). High-dielectric constant ceramics for base metal monolithic capacitors. *Jpn. J. Appl. Phys. Suppl.*, 20, 147.
- Simon-Seveyrat, L., Hajjaji, A., Emziane, Y., Guiffard, B. and Guyomar, D. (in press). (2006). Re-investigation of synthesis of $BaTiO_3$ by conventional solid state reaction and oxalate coprecipitation route for piezoelectric applications. *Ceram. Int.*
- Tang, X.G., Chew, K.-h. and Chan, H. L.W. (2004). Diffuse phase transition and dielectric tunability of $Ba(Zr_yTi_{1-y})O_3$ relaxor ferroelectric ceramics. *Acta Mater.*, 52, 5177.
- Ulrich, W., Georg, G., Ulrich, B., Sophie, W., Detlev, H. and Rainer, W. (2001). Dielectric properties of $Ba(Zr,Ti)O_3$ -based ferroelectrics for capacitor applications. *J. Am. Ceram. Soc.*, 84(4), 759.
- Vittayakorn, N., Rujijanagul, G., Tunkasiri, T., Xiaoli, T. and Cann, D.P. (2003). Perovskite phase formation and ferroelectric properties of the lead nickel niobate-lead zinc niobate-lead zirconate titanate ternary system. *J. Mater. Res.*, 18(12), 2882.
- Vittayakorn, N. Rujijanagul, G., Xiaoli, T., Meagen, A., Marquardt and Cann, D.P. (2004). The Morphotropic phase boundary and dielectric properties of the $xPb(Zr_{1/2}Ti_{1/2})O_3$ - $(1-x)Pb(Ni_{1/3}Nb_{2/3})O_3$ perovskite solid solution. *J. Appl. Phys.*, 96(9), 5103.
- Yu, Z., Ang, C., Guo, R. and Bhalla, A.S. (2002). Dielectric properties and high tunability of $Ba(Ti_{0.7}Zr_{0.3})O_3$ ceramics under dc electric field. *Appl. Phys.Lett.*, 81(7), 1285.